

Light and temperature effect on CO desorption during photothermal CO₂ hydrogenation over Pt/Al₂O₃

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Abstract: Visible light illumination has been widely applied to promote activity, selectivity and stability of traditional thermal catalysts. Nevertheless, the role of light irradiation during catalytic reactions is not well understood. In this work, Pt/TiO₂ and Pt/Al₂O₃ prepared by wet impregnation were used for photothermal CO₂ hydrogenation. They showed a similar photothermal effect. Hence, operando diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and density functional theory (DFT) calculations were conducted on Pt/Al₂O₃ to reveal more insight into the mechanism. The results indicated that CO desorption from Pt sites including step sites (Pt_{step}) or/and terrace site (Pt_{terrace}) is an important step during CO₂ hydrogenation to free the active Pt sites. Notably, light illumination and temperature affected CO desorption in different ways. The calculated adsorption energy of CO on Pt_{step} and Pt_{terrace} sites was -1.24 and -1.43 eV, respectively. Hence, CO is stronger bound to Pt_{step} sites. During heating process in the dark, CO preferentially desorbs from Pt_{terrace} site. However, the additional light irradiation facilitates transfer of CO from Pt_{step} to Pt_{terrace} sites and its subsequent desorption from the Pt_{terrace} sites, thus promoting CO₂ hydrogenation. This work provides further understanding of photothermal catalysis as a mechanism of promotion of the thermal reaction.

Key words: CO₂ hydrogenation; photothermal catalysis; Pt/Al₂O₃, operando DRIFTS, DFT

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1. Introduction

Emissions of carbon dioxide as a primary greenhouse gas result in global temperature increase and climate changes. Among the numerous CO₂ utilization strategies, CO₂ hydrogenation attracted extensive attention because it provides not only an important strategy for environmental improvement, but also a promising technology to produce renewable hydrocarbon fuels such as HCOOH, CH₃OH and CH₄ [1-3]. However, high temperature is generally required during CO₂ hydrogenation due to the thermodynamic stability of CO₂ [4-6].

Photothermal catalysis, a combination of photoexcitation with thermal energy to trigger chemical reactions, allows significant improvements in activity and selectivity of catalytic reactions as well as stability of the catalysts [1,7,8]. Therefore, light irradiation has been utilized to promote diverse thermal catalytic reactions such as CO oxidation [9], propylene oxidation [10], Fischer-Tropsch Synthesis [11], reverse water gas shift (RWGS) reaction [12] and CO₂ hydrogenation [13]. Light irradiation can significantly improve the performance during these reactions. In our previous work, we found that the light irradiation promoted CO oxidation through O₂ excitation [14]. In addition, Wang et al. reported that photo-induced back donation of electrons from Co to CO facilitated CO activation and dissociation [11]. Visible light irradiation increased RWGS activity of Au nanoparticles by 1300% while decreasing activation energy from 47 to 35 kJ·mol⁻¹ [12]. For CO₂ hydrogenation, light induced electron transfer from Rh to anti-bonding orbitals of a reaction intermediate resulted in efficient CH₄ generation [8]. CO desorption was named as the rate-limiting step during CO₂ hydrogenation [15]. However, the effects of light and temperature on this step are still not deeply understood.

In this work, CO₂ hydrogenation was conducted over Pt/TiO₂ and Pt/Al₂O₃ catalysts. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied to investigate CO desorption on Pt sites during photothermal CO₂ hydrogenation. The reaction pathway was discussed to develop the mechanism of photothermal catalysis.

2. Experimental

2.1. Catalyst synthesis

Pt/Al₂O₃ were prepared using wet impregnation with aqueous H₂PtCl₆ as described in our previous work [16]. γ -Al₂O₃ was bought from Aladdin Co., Ltd. 500 mg γ -Al₂O₃ was dispersed in a mixture of 5 mL H₂PtCl₆ (2 mg/mL) solution and 30 mL water to achieve 2 wt.% Pt loading on γ -Al₂O₃. Then the suspension was stirred for 6 h at 27 °C. The product was centrifuged and dried at 65 °C for 24 h. Pt/TiO₂ was prepared in the same way using hydrothermally synthesized anatase TiO₂ support as used by us earlier [14] and described in the Supporting Information.

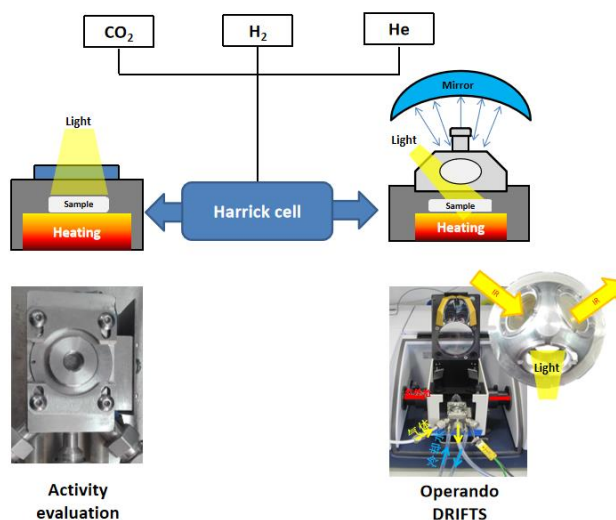
2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert diffractometer using Cu K α radiation operating at 40 mA and 40 kV. High resolution transmission electron microscopy (HRTEM) was carried out on a FEI Tecnai G2 20 microscope operating at 200 kV. UV-vis spectra were recorded on a Shimadzu 2600 UV-vis spectrophotometer. Raman spectra were obtained on a Horiba LabRAM HR Evolution with a 532 nm laser.

2.3 CO₂ hydrogenation evaluation and operando DRIFTS

Sieved powder catalysts (approx. 50 mg, sieve fraction: 100-200 μ m) were used for the tests. The catalysts were pretreated in 5% H₂/He (100 mL/min) at 200 °C for 6 h. The temperature of the catalyst bed was calibrated by an IR camera. During activity evaluations, 1000 ppm CO₂ and 6000 ppm H₂ in He were dosed into the reactor (Harrick Praying Mantis™ high temperature reaction chamber with a flat cover and a quartz window, Scheme 1, left) at 110 mL/min. Schott KL 2500 LCD light source (using 300 W Xe lamp) with an intensity of 710 mW/cm² was used as light source. CO and CO₂ concentrations were detected by a Hartmann & Braun Uras 10E detector. OmniStar GSD-320 quadrupole mass spectrometer (Pfeiffer Vacuum) was used to detect CO (m/z=28), CO₂ (m/z=44), CH₃OH (m/z=31), HCOOH (m/z= 46) and CH₄ (m/z=16).

For operando DRIFTS the gas composition was kept the same as for catalytic tests. The spectra were measured on a VERTEX 70 FTIR spectrometer (Bruker) equipped with a mercury cadmium telluride (MCT) detector. Harrick in situ cell with a dome cover with two KBr and a glass window was used as the reactor (Scheme 1, right). The catalyst was pretreated in 5% H₂/He with the flow rate of 100 mL/min at 200 °C for 6 h. The spectra of the pre-reduced catalysts at 30 °C in pure He gas were used as background spectra. The reaction conditions were stabilized for 30 min without light at room temperature, and then DRIFTS spectra were collected (without light) at 30, 80, 120, 160 and 200 °C. After the spectra obtained at each temperature point, the catalyst was irradiated during 10 min. Then it was first flushed with He and the spectra were recorded after the He flushing. At each temperature, the catalyst was flushed with He gas for 10 and 20 min, and then additional spectra were collected. IR scanning range was 4000 ~ 700 cm⁻¹ with 4 cm⁻¹ resolution and averaging over 100 scans.



Scheme 1. Scheme of the setup for CO₂ hydrogenation activity evaluation and operando DRIFTS investigation.

2.4 Thermodynamic calculation

Equilibrium concentrations of species obtained during CO₂ hydrogenation were calculated by HSC chemistry 7. The ratio of CO₂/H₂ was 1/6, CHOOH, CH₃OH, CO, H₂O and CH₄ were originally considered as products. Including CH₄ in the calculation led to the conclusion that is the preferred product under thermodynamic control with an equilibrium concentration near 100% among all carbon-containing species at all studied temperatures[17]. Since only a small amount of CH₄ was detected experimentally, its production is limited by kinetics. Therefore, it was excluded from further thermodynamic analysis.

2.5 Computational details

Density functional theory (DFT) calculations were performed using DMol³ procedure based on Materials Studio software. The electron exchange and correlation were approximated by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. Dispersion correction by TS (DFT-D) was used to describe the van der Waals interaction. The valence electron configurations were 2s²2p² for C, 2s²2p⁴ for O and 5d⁹6s¹ for Pt, respectively. As for the Monkhorst-Pack grid k-point in the Brillouin-zone, a 5×5×1 k-point was used for geometry optimizations. For convergence threshold, the total energy of the system, maxforce, and displacement tolerances were set to be 1 × 10⁻⁵ Ha, 0.02 Ha/Å, and 0.05 Å, respectively. A space of 15 Å vacuum was set between slabs in order to avoid interaction.

The adsorption energy (E_{ad}) of adsorbates was calculated as follows:

$$E_{ad} = E_{CO+surface} - E_{surface} - E_{CO},$$

where $E_{CO+surface}$ is the total energy of Pt surface with CO, $E_{surface}$ is the total energy of the clean surface, and E_{CO} is the total energy of CO in the gas phase. The CO molecule was optimized in a three-dimensional (3D) box of a=b=c=15 Å.

3. Results and discussion

3.1. Photothermal effect and the active site

CO₂ conversion rate and CO production rate during CO₂ hydrogenation over Pt/Al₂O₃ at different temperatures are depicted in Fig. 1. As shown in Fig. 1a, during thermal catalysis CO₂ conversion rate increased from 0 to 10 μmol*g⁻¹min⁻¹ when temperature changed from 80 to 120 °C, and up to about 225 μmol*g⁻¹min⁻¹ at 400 °C. CO was not detected until the temperature increased to 200 °C (Fig. 1b). Additional light irradiation significantly promoted both CO₂ conversion and CO production rates. For example, CO₂ conversion rate with light at 120 °C was about 50 μmol*g⁻¹min⁻¹ while it was only 10 μmol*g⁻¹min⁻¹ in the dark. CO production rate was about 0 μmol*g⁻¹min⁻¹ at 120 °C in the dark and about 15 μmol*g⁻¹min⁻¹ under light irradiation (Fig. 1b). The rates measured at other temperatures were also obviously promoted by light. Moreover, light irradiation decreased the temperature required for CO generation on Pt/Al₂O₃. CO production rate at 120 °C under light was close to the thermal activated CO production rate at 250 °C, and a similar trend was also observed for CO₂ conversion rates. Rate enhancement was used to evaluate the effect of light on thermal reaction, the enhancement reached the maximum value at 80 °C at about 9 times compared to the corresponding purely thermal CO₂ conversion rate. As the temperature rose, thermal-induced rate further increased while the photo-induced enhancement decreased, which may be due to mass-transfer limitations [15].

On the other side, temperature increase due to light irradiation should also be taken into consideration. In our previous work, although light intensity was 972 mW/cm², light irradiation increased the surface temperature by no more than 60 °C [14]. In this work, at lower light intensity 710 mW/cm², both CO₂ and CO rates over Pt/Al₂O₃ at 80 °C under light irradiation were much higher than the rates at 160 °C in the dark. Therefore, Pt/Al₂O₃ exhibited typical synergistic effect of photoexcitation and thermal energy. Since the used γ-Al₂O₃ support material is a typical insulator and could not take part in the electron transfer process under light irradiation, Pt provided active sites for CO₂ hydrogenation.

To investigate the support effect the alumina support was replaced by the typical photocatalyst, TiO₂. As shown in Fig. S1a, CO₂ conversion rate over Pt/TiO₂ increased from 10 to 250 μmol*g⁻¹min⁻¹ when temperature increased from 80 to 400 °C. These rates were also significantly promoted by light irradiation. For example, the CO₂ conversion rate was 50 μmol*g⁻¹min⁻¹ at 80 °C with light on while it was only about 10 μmol*g⁻¹min⁻¹ in the dark. Moreover, the light induced CO₂ conversion rate, 50 μmol*g⁻¹min⁻¹, was identical to the rate measured at 250 °C in the dark. The CO₂ conversion and CO production rates over Pt/TiO₂ were similar to those of Pt/Al₂O₃. The slightly higher activity of Pt/TiO₂ may be due to strong interaction between the Pt metal and TiO₂ support resulting in higher dispersion of Pt and inhibition of sintering [16]. Due to very small difference in catalytic activity of both catalysts and to exclude the photocatalytic effect of titania the following investigations of the mechanism of CO₂ hydrogenation on Pt sites were conducted on Pt/Al₂O₃.

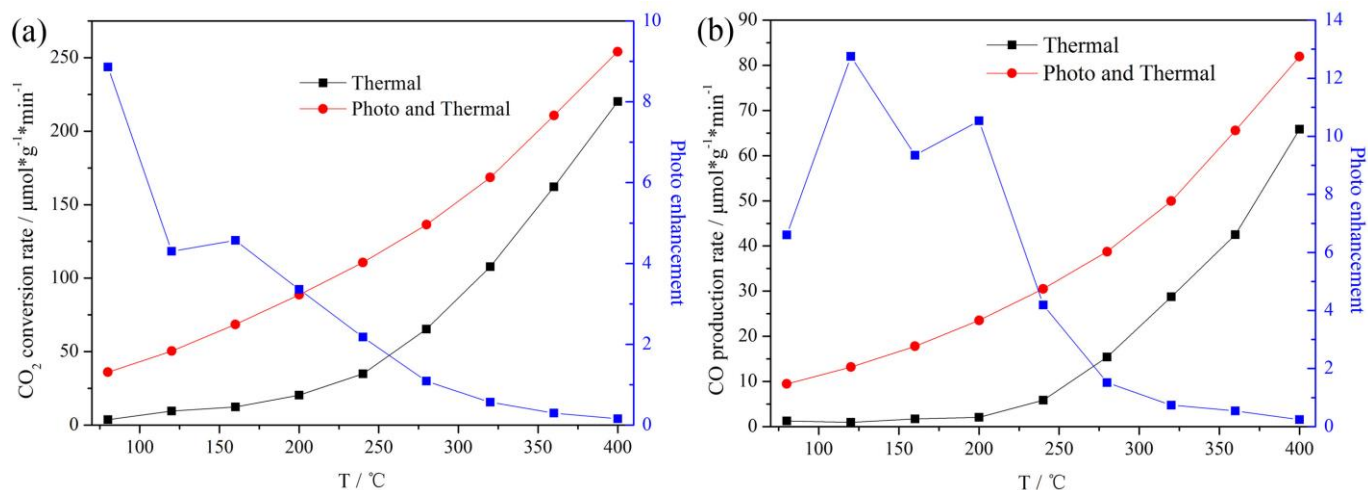


Fig. 1. a) CO₂ and b) CO conversion rates of photothermal CO₂ hydrogenation on Pt/Al₂O₃.

3.2. Products of CO₂ hydrogenation

According to Fig. 2a, the CO₂ conversion rate of Pt/Al₂O₃ increased from 32 to 75 μmol·g⁻¹·min⁻¹, and then decreased to 30 μmol·g⁻¹·min⁻¹ while the temperature increased from 80 to 400 °C. Meanwhile, CO production rate increased from 8 to 25 μmol·g⁻¹·min⁻¹ and then decreased to 15 μmol·g⁻¹·min⁻¹. Obviously, the consumed CO₂ was not totally converted into CO. To evaluate the composition of CO₂ hydrogenation products the outlet gas was analyzed by mass spectrometry (Fig. 2b) and the ion currents of some reactants and products are summarized in Fig. S2. Once CO₂ and H₂ feed was switched on higher H₂O, CH₄, and HCOOH background was detected. Further heating resulted in the corresponding increase in CH₄ and H₂O signals while CO₂ and HCOOH signals decreased. These results indicate that CO₂ and H₂ gradually converted into CH₄ and H₂O, and HCOOH may have been consumed as the reaction intermediate.

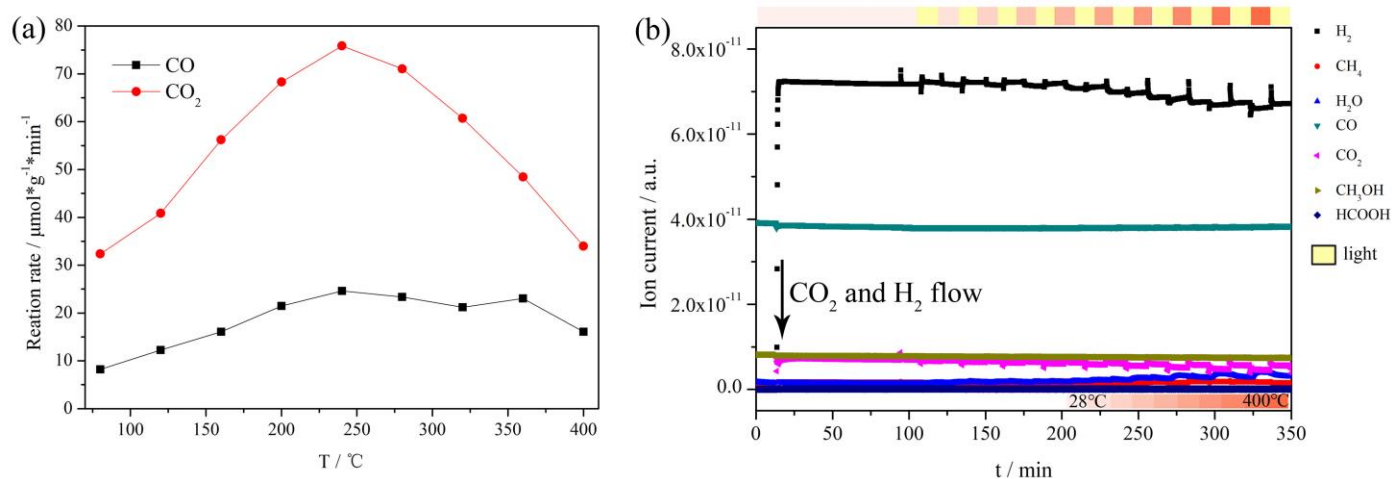


Fig. 2. a) CO₂ conversion and CO production rates of Pt/Al₂O₃ induced by light irradiation (after subtracting the corresponding thermally induced rates); b) Ion currents of products of CO₂ hydrogenation over Pt/Al₂O₃ measured at different temperatures in the dark and under light irradiation.

Thermodynamic equilibrium calculation for the used gas feed (molar ratio CO₂:H₂=1:6) is shown in

Fig. 3. Three ranges can be observed during heating process. Below 120 °C CH₃OH is the thermodynamically preferred product of CO₂ hydrogenation (note that CH₄, if included in the calculation, would be the most thermodynamically stable through the whole studied temperature range). Although HCOOH is thermodynamically less stable than the other products, it was experimentally detected and its concentration was decreasing with increasing temperature. In the range of 120 to 180 °C, CO₂ is the most thermodynamically stable component, hence its reduction is not favored in this temperature range, as was also confirmed experimentally giving the low conversion rates. When temperature was above 180 °C, CO₂ conversion rate gradually increased, and CO production (reverse water gas shift reaction) is favored, consistent with the experimental CO₂ and CO rates changes shown in Fig. 3a. As shown in Fig. S2, the ion currents of reactants and products obtained from experimental results exhibited similar trends to the calculation. Thus, the thermodynamic calculation agrees well with the experimental results, and these results indicated that CO₂ hydrogenation is not limited by kinetics (unlike the CH₄ pathway).

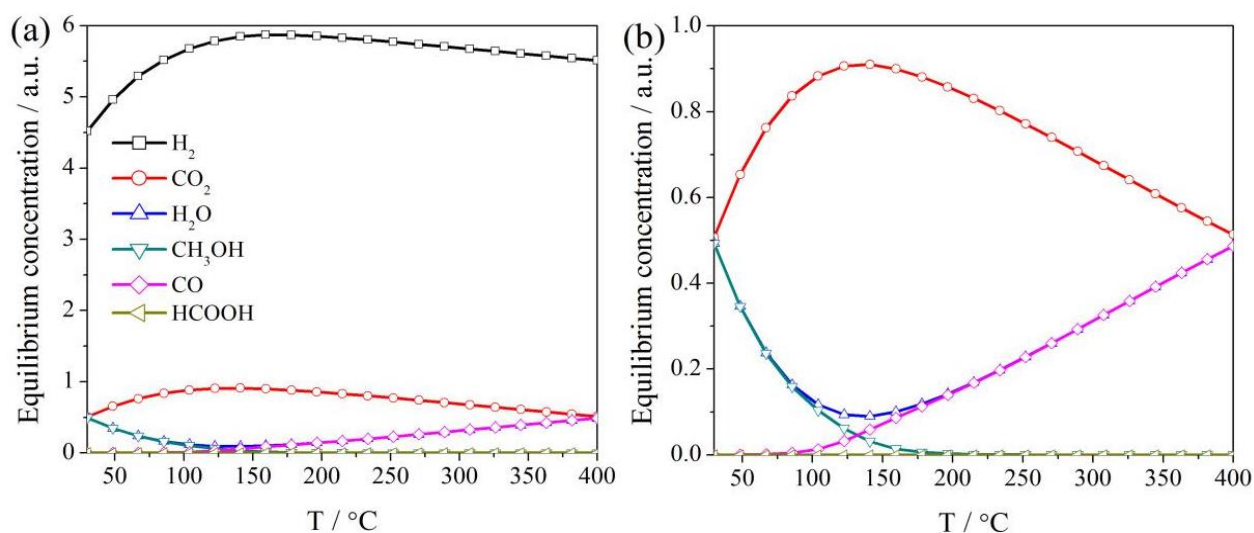


Fig. 3. Relative thermodynamic stability of species in the system including CO₂ (initial concentration 1), H₂ (initial concentration 6), and CO, HCOOH, CH₃OH, H₂O (initial concentrations of the four latter species were 0).

3.3. Structure, morphology and optical properties

Pt was not detected in the XRD patterns (Fig. 4a), and all diffraction peaks were attributed to γ -Al₂O₃ (PDF#16-0394). TEM images (Fig. 4b) showed only a few Pt nanoparticles with a diameter of approx. 10 nm deposited on Al₂O₃, and the crystalline interplanar spacing of 0.226 and 0.195 nm were indexed to {111} and {200} facets of Pt. As reflected by UV-vis spectra (Fig. S3), Pt deposition promoted the light adsorption ability of Al₂O₃ in the range of 200 ~ 600 nm [18]. For Pt/TiO₂, also the strong interaction at the Pt/TiO₂ interface was evidenced [16]. Raman spectra showed a signal located at 145 cm⁻¹ assigned to the E_g(1) peak of anatase (spectrum given in the supporting information, Figure S4). After Pt deposition, this peak shifted to 151 cm⁻¹ which indicated the generation of Pt-O_{vacancy}-Ti³⁺ at the interface between Pt and TiO₂ [19]. Hong et al. [ref] reported that Pt-O_{vacancy}-Ti³⁺ worked as an adsorption site for the reaction

intermediates, such as CO generated from HCOOH decomposition. This increased residence time of surface intermediates resulting in the promoted activity [20]. It might be also the reason that Pt/TiO₂ (Fig. S1) exhibited higher activity than Pt/Al₂O₃ (Fig. 1).

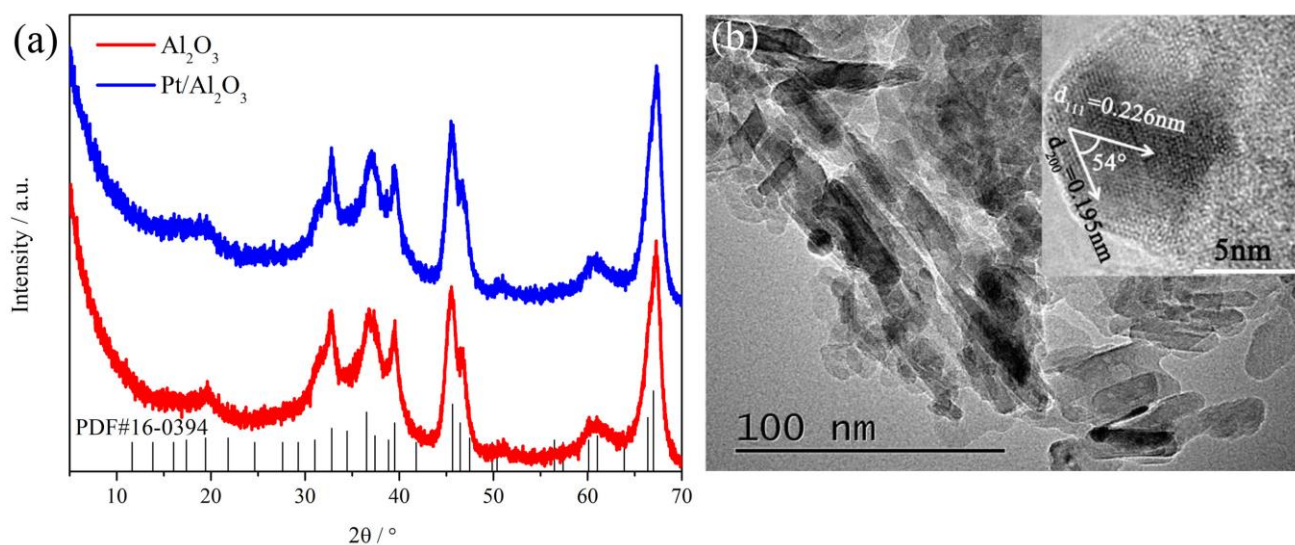


Fig. 4. a) XRD patterns and b) TEM images of Pt/Al₂O₃.

3.4. Operando DRIFTS

Operando DRIFTS spectra measured during photothermal catalytic CO₂ hydrogenation are shown in Fig. 5 and the assignments of IR peaks are summarized in Table 1. The maximum temperature was 200 °C to obtain reasonable signal-to-noise ratio.

Table 1 Assignments of peaks in IR spectra during CO₂ hydrogenation

Wavenumber/ cm ⁻¹	Assignment	Reference
2326 ~ 2362	CO ₂	[21]
2058 ~ 2046	CO Pt _{terrace}	[22,23]
2038 ~ 2007	CO Pt _{step}	[22][23]
2007	Carbonyls on Pt or CO on Pt _{step}	[23][24]
1760	Bridged CO	[22]
1625	-OH	[23,25]

As shown in Fig. 5a, after exposure of Pt/Al₂O₃ to CO₂ and H₂ at 30 °C peaks emerged at 2326 ~ 2362 and 1625 cm⁻¹ which were attributed to CO₂ and -OH on Pt [21,23,25]. These signals became weaker and peaks at 2007 and 1760 cm⁻¹ corresponding to carbonyl and CO evolved as temperature increased from 30 to 200 °C [22-24]. During temperature increase to 120 °C CO production was not observed (Fig. S2d) in

agreement with thermodynamics (Fig. 3b) while HCOOH decreased (Fig. S2e) and the intensity of carbonyl band at 2007 cm^{-1} (Fig. 5a) did not increase. Increase in the catalyst temperature resulted in higher intensity of the carbonyl band at 2007 cm^{-1} . Considering the gradual decrease of HCOOH concentration in the effluent (Fig. S2e) and increase CO concentration (in Fig. 1, Fig. 2 and Fig. 3), the higher band intensity was attributed to the CO produced on Pt_{step} site [22,23].

Under light illumination below $80\text{ }^{\circ}\text{C}$ the intensity of 1624 cm^{-1} band (surface -OH) decreased (Fig. 5b), and the signals in the range of $2326 \sim 2362\text{ cm}^{-1}$ (CO_2) slightly increased while the peaks at 2007 cm^{-1} and 1760 cm^{-1} (CO) obviously rose [21-24]. Besides, CO_2 and HCOOH ion currents decreased as shown in Fig. S2a and Fig. S2e. These changes indicate that CO_2 preferred to adsorb on Pt and then form small amount of CO under light irradiation. At temperatures above $120\text{ }^{\circ}\text{C}$ CO generation was promoted by temperature and CO molecules gradually accumulated on Pt_{step} sites without light. With light turned on at the respective temperatures CO signals were significantly increased indicating the promoted CO generation (Fig. 5b), in accordance with increased concentration of CO in the gas phase (Fig. 1b and Fig. S2d). Noteworthy, the CO signal at 2007 cm^{-1} was blue shift once the light was turned on indicating that interaction of CO molecules with Pt_{step} sites weakened.

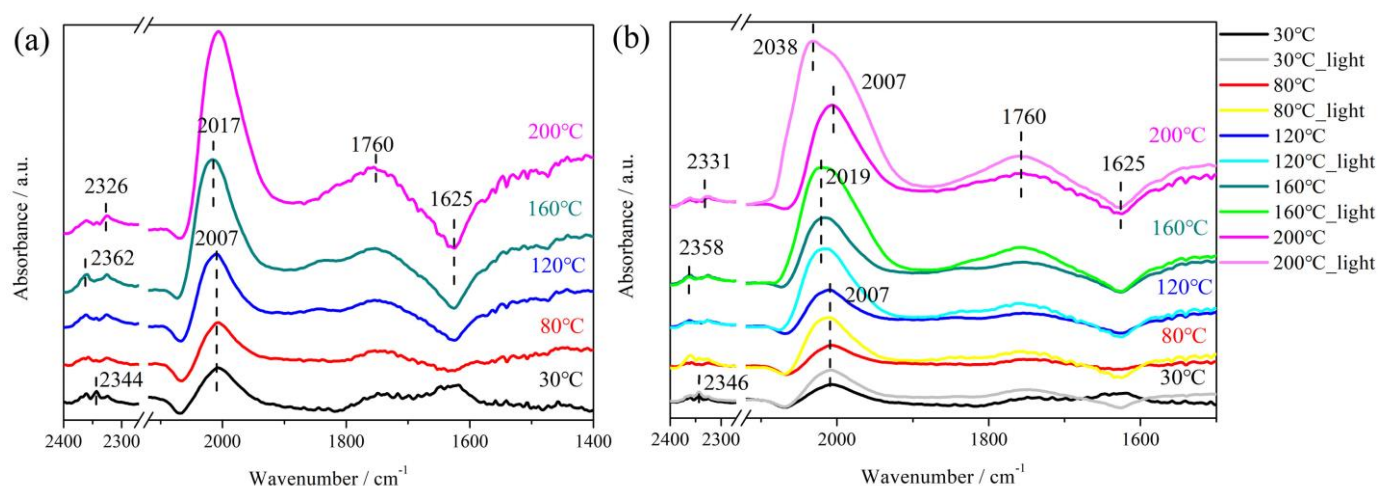


Fig. 5. Operando DRIFTS spectra of $\text{Pt}/\text{Al}_2\text{O}_3$ during a) thermal and b) photothermal CO_2 hydrogenation

To further investigate the interaction between CO and Pt helium was used to flush the catalyst surface to observe the intermediate species adsorbed during photothermal CO_2 hydrogenation (Fig. 6). CO on Pt_{step} sites ($2038 \sim 2007\text{ cm}^{-1}$ [22,23]) was not visible after He flushing. But CO on $\text{Pt}_{\text{terrace}}$ sites was detected in the range of $2058 \sim 2046\text{ cm}^{-1}$ different to the thermal catalysis shown in Fig. 5a [22,23]. That indicates that light and temperature have different effects on CO adsorption. CO adsorbs on Pt_{step} sites much stronger compared to $\text{Pt}_{\text{terrace}}$ sites, desorption from which was found to occur at approx. $350\text{-}450\text{ K}$ [26]. As shown in Fig. 1b, small amount of CO evolved at temperature below $200\text{ }^{\circ}\text{C}$ in the dark, hence the generated CO probably desorbed from $\text{Pt}_{\text{terrace}}$ sites and the corresponding signals could not be observed in the IR spectra (Fig. 5a). On the other hand, CO was adsorbed stronger on undercoordinated Pt_{step} sites resulting in clearly visible IR bands. Even when the temperature reached $200\text{ }^{\circ}\text{C}$ the produced CO was still accumulated on

Pt_{step} sites as reported in previous research [27]. Thus, the observed CO on Pt_{terrace} in Fig. 6 was not originating during thermal catalysis but during light irradiation.

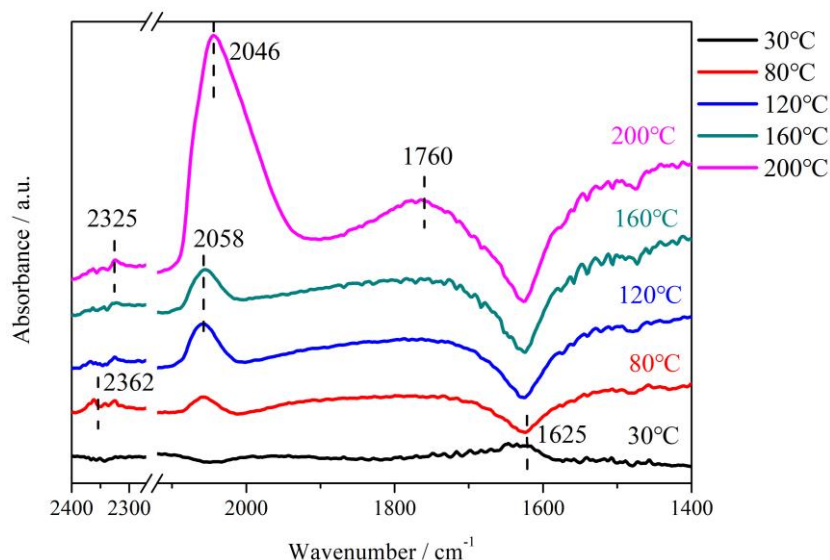


Fig. 6. Operando DRIFTS spectra of Pt/Al₂O₃ with 20 min flushing with He gas after turning off light

3.5. Effects of light and temperature on CO₂ desorption

According to the mechanism of CO₂ hydrogenation [28], CO desorption is regarded as the rate-limiting step with activation energy of CO desorption from Pt and Pd much higher than from other metals [15]. At low temperatures the active sites on metal surface are usually covered by CO which poisons or blocks the sites [29,30]. Hence, CO desorption from the active sites is required to free sites catalyzing CO₂ hydrogenation. The operando DRIFTS results indicated that light and temperature affected CO desorption in different ways. Formed CO preferred to desorb from Pt_{terrace} sites during heating while its distribution seem to be altered under additional light irradiation.

Compared to the terrace sites, metal step sites are more coordinatively more unsaturated which is beneficial for CO adsorption [31,32]. To further reveal the interaction between CO and Pt, energies of CO adsorption on Pt_{terrace} and Pt_{step} sites were calculated by DFT. Adsorption geometries and the corresponding energies are shown in Fig. 7. Pt-C distances for CO adsorbed on Pt_{terrace} and Pt_{step} sites were 2.01 and 1.98 Å and the adsorption energies were -1.24 and -1.43 eV, respectively. This indicates that CO adsorbs stronger on Pt_{step} sites than Pt_{terrace} sites, consistent with IR results [33,34]. As shown in Fig. 5b and Fig. 6, light irradiation weakens the interaction between CO and Pt_{step} sites. But, even after helium flushing CO on Pt_{terrace} site with weaker bonding was still detected during the photothermal process in the range of 30 ~ 200 °C while the CO on Pt_{step} site was not visible. This indicates that CO desorbed from Pt_{step} sites while the produced CO accumulated on Pt_{terrace}. Additionally, Lawrenz et al. [35] reported that laser light could induce the spillover of CO from Pt_{step} to Pt_{terrace} sites. Thus, with the light irradiation, produced CO first transfers from Pt_{step} sites to Pt_{terrace} sites and then desorbs from Pt_{terrace} sites.

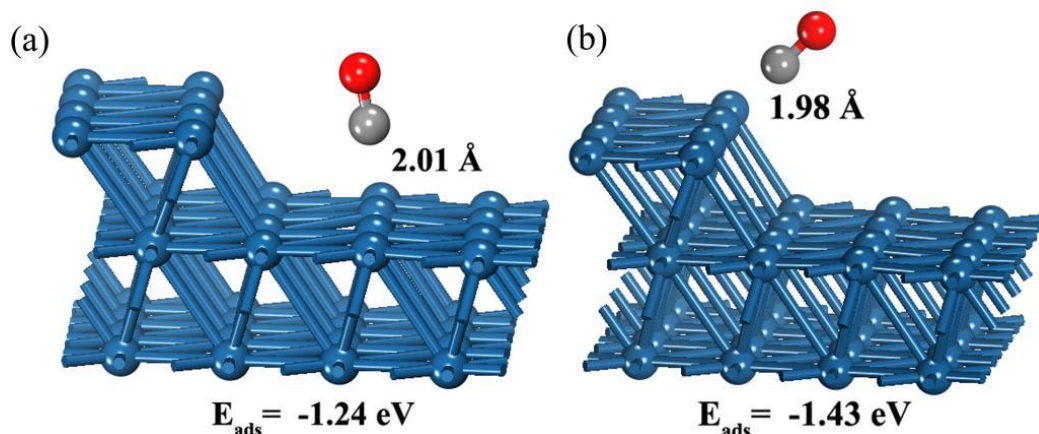


Fig. 7. Adsorption energies and Pt-C distances for CO adsorbed on a) Pt_{terrace} and b) Pt_{step}

Based on the results mentioned above, the mechanism of light and temperature activation of CO desorption from Pt during CO₂ hydrogenation is summarized in Fig. 8. CO₂ and H₂ are spontaneously converted to HCOOH due to the low activation energy [36]. Subsequently, HCOOH is decomposed to CO adsorbed on Pt_{terrace} ($E_{\text{ads}} = -1.24 \text{ eV}$) and Pt_{step} ($E_{\text{ads}} = -1.43 \text{ eV}$) sites. CO desorption is regarded as a crucial step during CO₂ hydrogenation to free the active low-coordinated Pt step sites. Considering the weaker interaction between CO and Pt_{terrace} sites, generated CO preferred to desorb from Pt_{terrace} site in thermally activated CO₂ hydrogenation process [27]. On the contrary, additional light irradiation induced CO desorption from Pt_{step} sites (with possible spillover to Pt_{terrace} sites) as evidenced by operando DRIFTS. As a result, the interaction between CO and Pt site became weaker and further thermally activated CO desorption from Pt_{terrace} site was facilitated. Hence we suggest that this, in turn, promotes CO₂ hydrogenation [35,37], which should be further substantiated in future studies.

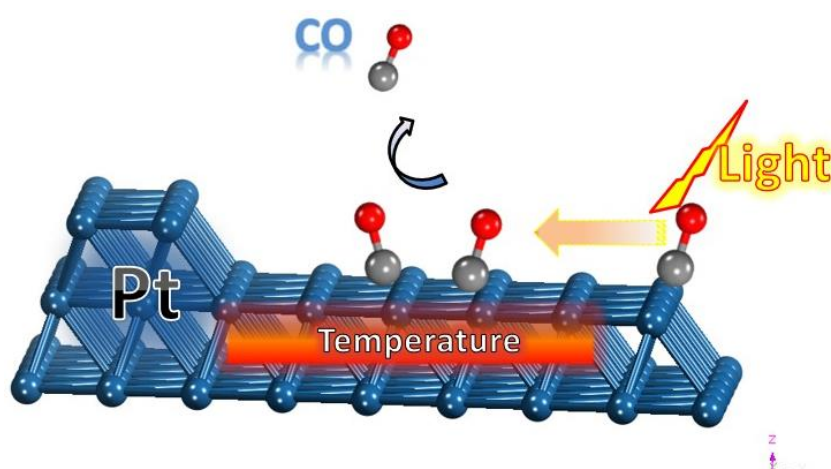


Fig. 8. Light and temperature effect on the CO desorption during CO₂ hydrogenation on different Pt sites

4. Conclusions

Pt/Al₂O₃ was synthesized through impregnation method. It exhibited photothermal catalytic activity in CO₂ hydrogenation with Pt providing active sites. Operando DRIFTS and theoretical calculations indicated that light and temperature facilitated CO desorption from Pt in different ways. CO preferentially desorbed from Pt_{terrace} sites during thermal activation. With the additional light irradiation, CO on Pt_{step} site transferred to Pt_{terrace} site, and then desorbed. As a result, CO desorption activated by both heating process and additional light irradiation resulted in the promotion of CO₂ hydrogenation. This work provides further understanding of the effect of light and temperature on CO desorption during CO₂ hydrogenation, and may help in designing more efficient photothermal catalytic processes in future.

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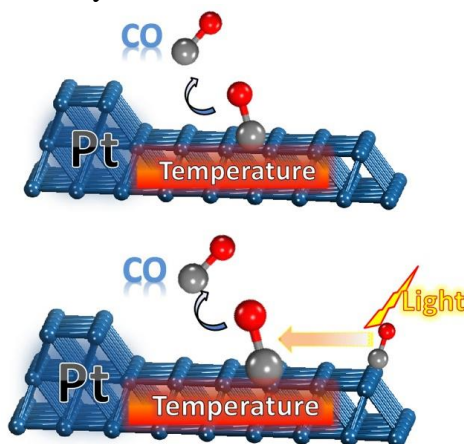
Graphical Abstract

The manuscript title

Light and temperature effect on CO desorption during photothermal CO₂ hydrogenation over Pt/Al₂O₃

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Light illumination and temperature affected CO coverage during CO₂ hydrogenation in different ways, offering a new pathway for improving thermal catalysis.